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ELECTRODEPOSITION OF SILVER ONTO A SINGLE-CRYSTAL Ag(111) PLANE FROM A CYANIDE BATH IN THE PRESENCE OF CHLORIDE IONS

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Summary

Observations were made of silver electrodeposited onto the (111) plane of a silver single crystal from a complex cyanide bath. In the presence of chloride ions the growth habit of the silver is modified for deposition at low current densities, *i.e.* at 2 and 5 mA cm^{-2}. At 7.5 and 10 mA cm^{-2} the deposit is nodular and rough in the presence of chloride ions. At 15 mA cm^{-2} high chloride ion concentrations produce cathodic hydrogen evolution, resulting in a fern-like deposit.

1. Introduction

Addition agents in electroplating baths are known to have marked effects on the physical properties of electrodeposits. However, despite the extensive use of addition agents, their functioning is little understood. The best approach towards obtaining a proper understanding of the role of addition agents is to study the morphology of electrodeposits grown on single-crystal planes with and without addition agents. The knowledge thus gained, combined with an evaluation of electrode kinetic parameters such as i_0 and b, may give a correct understanding of the effects of these agents. Work along these lines has been done by several researchers [1 - 5]. The effect of halide ions on the morphology of copper electrodeposits on copper single-crystal planes [6, 7] and the effect of chloride ions on silver electrodeposited onto a polycrystalline silver surface from a cyanide bath have been reported [8]. It is also known that the chloride ion has a higher polarizability than the cyanide ion [9]; it may thus be strongly adsorbed on the cathode surface, thereby producing changes in the kinetic parameters and in the growth habit.

With this in view, we studied the effect of chloride ions on the morphology and kinetic parameters of silver deposited from a complex cyanide bath at various current densities.

2. Experimental

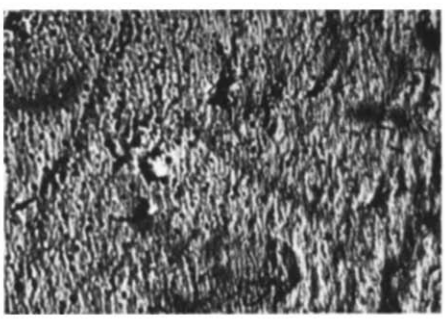
The experimental details have been described in detail elsewhere [10]. The solutions were prepared in conductivity water. The (111) plane was first mechanically polished on 3/0 and 4/0 emery paper using ethyl alcohol as lubricant. The crystal was then electropolished in an argentocyanide bath containing 35 g l^{-1} AgCN, 30 g l^{-1} KCN and 38 g l^{-1} K_2CO_3, as suggested by Shuttleworth *et al.* [11] but at a constant cell potential of 0.9 V instead of the 1.6 V that they suggested. The polished surface was washed immediately with distilled water and the crystal was then transferred to an electrolytic cell containing the required amount of KCl in a complex cyanide bath. The electrolytic bath solution consisted of 33.5 g l^{-1} AgCN, 35 g l^{-1} KCN and 38 g l^{-1} K_2CO_3. The overpotential was measured with reference to a freshly prepared silver electrode to an accuracy of ± 10 mV using a pH meter. The surface of the silver deposit was examined under a metallurgical microscope and micrographs were taken.

3. Results

3.1. Morphology

3.1.1. At 2 mA cm^{-2}

A ridge type of deposit was obtained when silver was deposited from the pure complex cyanide bath at 2 mA cm^{-2} (Fig. 1). The addition of chloride ions had no effect on the morphology of the deposit up to a concentration of 10^{-8} mol l^{-1} but at 10^{-7} mol l^{-1} Cl^- the deposit consisted of layers with striations (Fig. 2). A further increase in the chloride ion concentration had a levelling effect on the deposit. At 10^{-4} mol l^{-1} Cl^- pyramids were formed (Fig. 3) and at 10^{-1} mol l^{-1} a ridge type of growth with pitting was observed (Fig. 4).



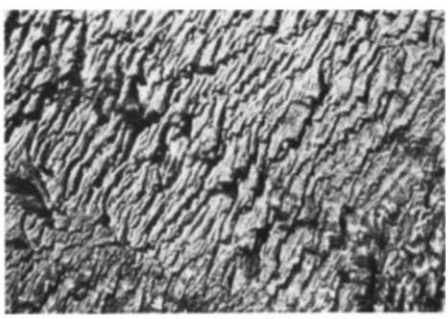


Fig. 1. Ridges of silver deposited onto Ag(111) from a pure cyanide bath at 2 mA cm^{-2}. (Magnification, 500 ×.)

Fig. 2. Layers with striations deposited onto Ag(111) in the presence of 10^{-7} mol l^{-1} Cl at 2 mA cm^{-2}. (Magnification, 500 ×.)

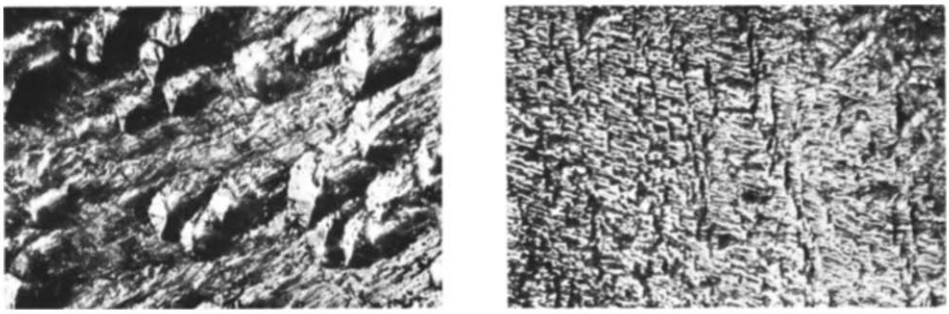


Fig. 3. Pyramidal growth of silver deposited onto Ag(111) in the presence of 10^{-4} mol l^{-1} Cl^- at 2 mA cm^{-2}. (Magnification, 500×.)

Fig. 4. A silver deposit obtained on Ag(111) in the presence of 10^{-1} mol l^{-1} Cl^- at 2 mA cm^{-2}. (Magnification, 500×.)

3.1.2. At 5 mA cm^{-2}

A polycrystalline deposit was obtained when silver was deposited from the pure bath (Fig. 5). A slight refinement in the grain size of the deposit was observed with the addition of chloride ions to the bath. The morphology of the deposit remained almost the same with increased chloride ion concentrations. A uniform bright deposit was obtained in the presence of 10^{-1} mol l^{-1} Cl^- (Fig. 6).

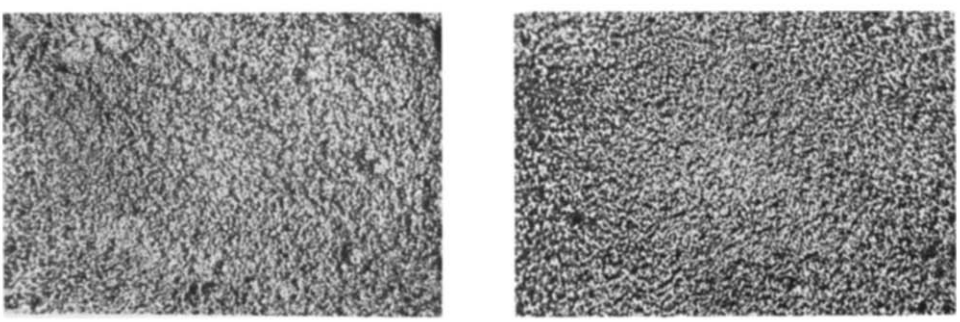
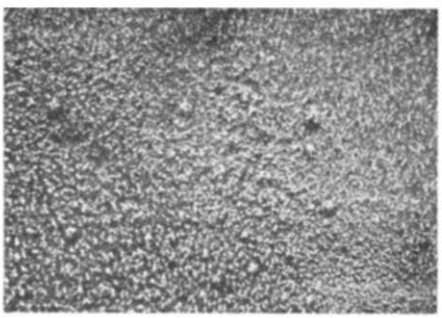


Fig. 5. Polycrystalline silver deposited onto Ag(111) from a pure cyanide bath at 5 mA cm^{-2}. (Magnification, 500×.)

Fig. 6. A bright uniform polycrystalline deposit obtained on Ag(111) in the presence of 10^{-1} mol l^{-1} Cl^- at 5 mA cm^{-2}. (Magnification, 500×.)

3.1.3. At 7.5 mA cm^{-2}

A fine-grained polycrystalline deposit was obtained when silver was deposited at 7.5 mA cm^{-2} from the pure complex cyanide bath (Fig. 7). The addition of chloride ions produced a rough non-uniform deposit. Small irregular pyramids on a polycrystalline background were observed when silver was deposited at higher chloride ion concentrations (Fig. 8).



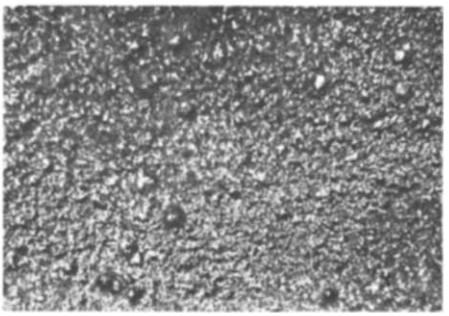
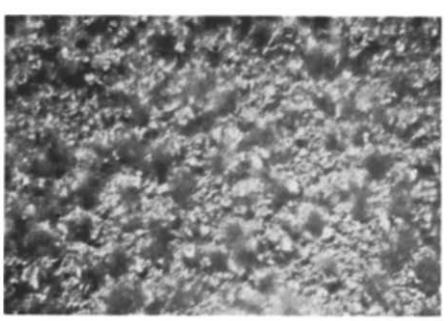


Fig. 7. Fine-grained polycrystalline silver deposited onto Ag(111) from a pure cyanide bath at 7.5 mA cm $^{-2}$. (Magnification, 500 × .)

Fig. 8. Small irregular pyramids on silver deposited onto Ag(111) in the presence of 10^{-3} mol l^{-1} Cl$^-$ at 7.5 mA cm $^{-2}$. (Magnification, 500 × .)

3.1.4. At 10 mA cm $^{-2}$

Irregular pyramidal growth on a polycrystalline background was observed when silver was deposited at 10 mA cm $^{-2}$ from the pure complex cyanide bath. On increasing the concentration of chloride ions from 10^{-10} to 10^{-6} mol l^{-1} the number of irregular pyramids on the non-uniform deposit increased (Fig. 9). A further increase in chloride ion concentration increased the pyramidal growth on the deposit still further. At 10^{-1} mol l^{-1} Cl$^-$ a fern-like deposit was observed (Fig. 10).



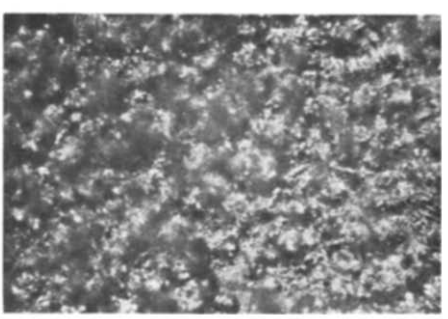


Fig. 9. More numerous (*cf.* Fig. 8) pyramids on a polycrystalline background deposited onto Ag(111) in the presence of 10^{-6} mol l^{-1} Cl$^-$ at 10 mA cm $^{-2}$. (Magnification, 500 × .)

Fig. 10. Silver deposited onto Ag(111) in the presence of 10^{-1} mol l^{-1} Cl$^-$ at 10 mA cm $^{-2}$. (Magnification, 500 × .)

3.1.5. At 15 mA cm $^{-2}$

Nodular polycrystalline growth was observed when silver was deposited from the pure bath (Fig. 11). At a concentration of 10^{-3} mol l^{-1} Cl$^-$ cathodic hydrogen evolution was observed, resulting in a fern-like deposit (Fig. 12). Higher chloride ion concentrations produced a similar effect.

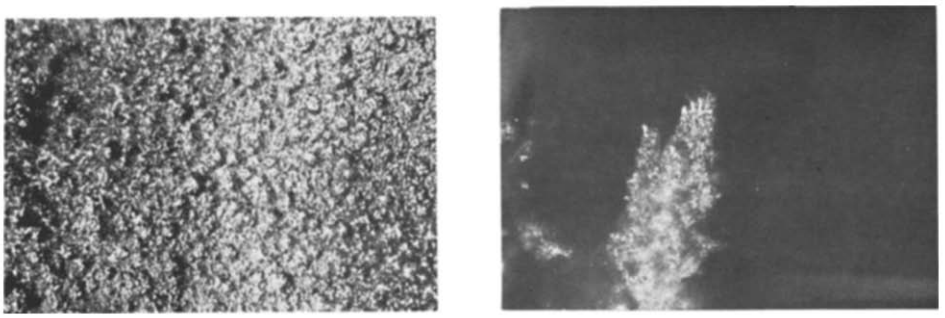


Fig. 11. Nodular polycrystalline silver deposited onto Ag(111) from a pure cyanide bath at 15 mA cm $^{-2}$. (Magnification, 500 ×.)

Fig. 12. A fern-like deposit obtained on Ag(111) in the presence of 10 $^{-3}$ mol l $^{-1}$ Cl^- at 15 mA cm $^{-2}$. (Magnification, 500 ×.)

3.2. Overpotential

The overpotentials at all current densities both in pure solution and in the presence of chloride ions remained steady with time. The overpotential increased with increasing chloride ion concentration. Hydrogen evolution at the cathode was observed only when the overpotential was greater than 0.8 V. The Tafel plots (Fig. 13) showed an increase in i_0 with increasing chloride ion concentration, indicating a decrease in the rate of deposition.

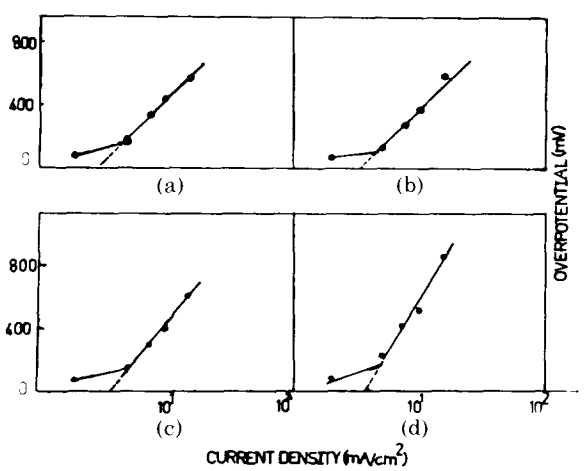


Fig. 13. Overpotential *vs.* current density for the electrodeposition of silver onto Ag(111) from a pure cyanide bath and a cyanide bath containing various concentrations of chloride ions: (a) pure solution, b = 0.78 V, i_0 = 3.0 mA cm $^{-2}$; (b) cyanide solution containing 10 $^{-9}$ mol l $^{-1}$ Cl^-, b = 0.80 V, i_0 = 3.4 mA cm $^{-2}$; (c) cyanide solution containing 10 $^{-4}$ mol l $^{-1}$ Cl^-, b = 1.0 V, i_0 = 3.6 mA cm $^{-2}$; (d) cyanide solution containing 10 $^{-1}$ mol l $^{-1}$ Cl^-, b = 1.4 V, i_0 = 3.8 mA cm $^{-2}$.

4. Discussion

From the Tafel relations it can be seen that i_0 increases with increasing overpotential. Hence we conclude that the rate of deposition is retarded by chloride ions. It is known that the chloride ion has a higher polarizability than the cyanide ion: 890 mm^2 mol^{-1} compared with 840 mm^2 mol^{-1} [9]. Hence chloride ions could replace either one or both of the cyanide ligands in the argentocyanide complex resulting in a change in the kinetic parameters. Furthermore, because of their high polarizability chloride ions have a tendency to adsorb on the cathode. Thus the observed changes in the kinetic parameters and the morphology are probably due to the high polarizability of the chloride ion.

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